

# INTEGRAL CATALYTIC COMBUSTION/FUEL REFORMING FOR GAS TURBINE

*Prepared For:*

**California Energy Commission**  
Energy Innovations Small Grant Program

*Prepared By:*

University of Maryland

**FEASIBILITY ANALYSIS AND FINAL EISG REPORT**

May 2005  
CEC-500-2005-078

# **ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM**

## **FEASIBILITY ANALYSIS REPORT (FAR)**

### **INTEGRAL CATALYTIC COMBUSTION/FUEL REFORMING FOR GAS TURBINE CYCLES**

#### **EISG AWARDEE**

University of Maryland  
Dept. of Mechanical Engineering  
College Park, MD  
Phone: (301) 405-2368  
Email: gsjackso@eng.umd.edu  
Principal Investigator: Prof. Greg S. Jackson

#### **AUTHOR**

EISG Program Administrator

Grant #: 99-21  
Grant Funding: \$74,992  
Term: July 1, 2000 – November 30, 2002  
PIER Subject Area: Environmentally Preferred Advanced Generation

## **LEGAL NOTICE**

This report was prepared as a result of work sponsored by the California Energy Commission (Commission). It does not necessarily represent the views of the Commission, its employees, or the state of California. The Commission, the state of California, its employees, contractors, and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the use of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the Commission nor has the Commission passed upon the accuracy or adequacy of the information in this report.

## **PREFACE**

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million of which \$2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University, which is under contract to the Commission.

The EISG Program conducts four solicitations a year and awards grants up to \$75,000 for promising proof-of-concept energy research.

PIER funding efforts are focused on the following six RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

The EISG Program Administrator is required by contract to generate and deliver to the Commission a Feasibility Analysis Report (FAR) on all completed grant projects. The purpose of the FAR is to provide a concise summary and independent assessment of the grant project using the Stages and Gates methodology in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions (as presented in the Independent Assessment section).

The FAR is organized into the following sections:

- Executive Summary
- Stages and Gates Methodology
- Independent Assessment
- Appendices
  - Appendix A: Final Report (under separate cover)
  - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the FAR, please visit the EISG program page on the Commission's Web site at:

<http://www.energy.ca.gov/research/innovations>

or contact the EISG Program Administrator at (619) 594-1049 or email [eisgp@energy.state.ca.us](mailto:eisgp@energy.state.ca.us).

For more information on the overall PIER Program, please visit the Commission's Web site at <http://www.energy.ca.gov/research/index.html>.

# **Integral Catalytic Combustion/Fuel Reforming for Gas Turbine Cycles**

## **EISG Grant # 99-21**

Awardee:	University of Maryland
Principal Investigator:	Prof. Greg S. Jackson
PI Contact Info:	Phone: (301) 405-2368;
Email	gsjackso@eng.umd.edu
Grant Funding:	\$74,992
Grant Term:	July 2000 – November 2002

### **Introduction**

The purpose of this project was to establish the basis for developing an integral catalytic combustor/steam reformer for producing H<sub>2</sub>-rich reformat from natural gas while providing low NO<sub>x</sub> air to a gas turbine. Applications include stabilization of ultra-low NO<sub>x</sub> gas turbine combustors, pre-reforming fuel for solid oxide fuel cells, and consuming hydrogen-rich anode off-gas. Through solid-state heat conduction the integral catalytic combustor/steam reformer transfers heat from the catalytic combustion catalyst to the reforming catalyst. This reactor design allows combustion at high equivalence ratios and very high heat transfer rates to the reforming catalysts. These conditions enable conventional steam reformers to operate at standard temperatures, below 800°C. In this project the researcher optimized combinations of combustion and reforming catalysts in a laboratory-scale, flat-plate reactor. The researcher tested the catalyst combinations at atmospheric pressure to assess reactor operability.

These tests were also used to validate numerical models with detailed chemistry to establish the basis for reactor design and performance at the high-pressure conditions expected in actual applications. The project objectives included the development of a prototype reactor from these initial efforts. However, challenges in identifying stable catalyst combinations in the flat-plate reactor tests delayed the project and the prototype reactor was not built. Nonetheless, the project results provide a solid basis for the design and testing of a prototype reactor for ultra-low emissions combustion systems for gas turbines and fuel cell applications.

The researcher focused on the assessment of catalysts, design approaches, and reactor operability. The assessment was performed through the flat-plate reactor tests and numerical models validated with the flat-plate reactor data. The flat-plate reactor provided a simple geometry for assessing catalyst performance and heat transfer data to determine the necessary features of a full-scale reactor design.

### **Objectives**

The goal of this project was to determine the feasibility of an integral catalytic combustor/steam reformer for producing H<sub>2</sub>-rich reformat for ultra-low NO<sub>x</sub> gas turbines from natural gas. The researchers established the following project objectives:

1. Identify preferred reliable catalyst combinations.
2. Test selected catalyst combination in flat-plate reactor to assess reactor performance.
3. Develop models for integral catalytic combustor/reformer design and operability.
4. Assemble and test a sub-scale prototype of integral reactor at high-pressure conditions.

5. Analyze reactor performance in advanced fuel cell/gas turbine cycles.

### **Outcomes**

1. The researcher determined that high-activity reforming catalysts are needed (Rhodium (Rh)-based supported catalysts) to minimize the risk for thermal runaway of the catalytic combustion process. The high-activity Rh-based reforming catalysts provide adequate rates for endothermic steam reforming on one side of the reactor wall to permit catalytic combustion at relatively high fuel/air ratios. Without the heat transfer to the reforming catalyst, the catalytic combustion at high fuel/air ratios could result in over-temperature on the combustion catalyst surface. Rh-based reforming catalysts provide the necessary activity to sustain high conversion of  $\text{CH}_4$  to  $\text{H}_2$  at temperatures  $< 800^\circ\text{C}$  and thereby control combustion catalyst temperatures. Palladium (Pd) catalysts were chosen for the combustion side.
2. Flat-plate reactor tests demonstrated enhanced operability and low-temperature performance with  $\text{H}_2$  combustion in comparison to  $\text{CH}_4$  combustion using the preferred Pd-based combustion catalysts. These tests were performed with Rh reforming catalysts in the same reactor. For gas turbine applications, experimental results suggest the use of an integral reactor to convert a fraction of a  $\text{CH}_4$  fuel stream to  $\text{H}_2/\text{CO}$  would require a higher temperature combustion catalyst. However that catalyst should be less prone to deactivation than conventional Pd-based catalysts and require less low-temperature activity for reactor start-up
3. The numerical model established the operating parameters for operation under high-pressure conditions.
4. No prototype reactor was built. The researcher ran into time and fund constraints.
5. The results establish the potential for the integral reactor for sustaining catalytic combustion at low temperatures and for providing good volumetric efficiency for  $\text{H}_2$  production.

### **Conclusions**

1. The researcher identified an effective catalyst system for the integral steam reformer/catalytic combustor. The cost of the Rhodium catalyst may limit application of this system.
2. The integral reactor is well suited for burning fuel cell anode exhaust in fuel cell/gas turbine cycles.
3. The numerical model is available for commercial developers.
4. The next advance of this technology must include building and testing a prototype reactor.
5. The flat-plate reactor experiments and the associated numerical models identified the ratio of moles of combustion fuel to moles of reforming fuel necessary to establish reliable steady-state reactor performance within catalyst temperature limits. The results also indicate the best reactor design would involve a co-flow system where the high combustion and reforming rates occur near the entrance to the reactor

### **Benefits to California**

The ultimate success of this project in demonstrating operability of an integral reactor with stable catalyst temperatures for gas turbines with ultra-low emissions may provide a unique approach for gas turbines within California to set new “Best Available Control Technology” (BACT) standards. Successful development of the proposed integral catalytic combustor/steam reformer for natural gas will also provide technical expertise within the state for the emerging areas of

solid oxide and molten carbonate fuel cell power plants. While it is difficult to quantify the future market for high temperature fuel cells and ultra-low emission gas turbines, it is clear that ultra-clean power generation will be required in California by 2007. The development of the integral reactor concept may provide a critical enabling technology for those power plants.

### **Recommendations**

Development of a prototype integral catalytic combustor/steam reformer for natural gas was not completed as proposed, but the project results and the design tools developed in this project provide the basis for completion. The experimental and numerical results establish the reactor as a viable approach for burning fuel cell exhaust to make additional H<sub>2</sub> for fuel cell operation. Based on the outcomes from this preliminary evaluation of this reactor concept, recommendations for further development are:

1. Demonstrate a prototype reactor at pressures of 5 atm or higher.
2. Investigate the possibility of using new Pd-doped hexa-aluminate catalysts for operating temperatures > 900°C with CH<sub>4</sub> as the combustion fuel.
3. Test for durability of preferred catalyst combinations at operating conditions.
4. Develop a reactor operation strategy for fuel cell/gas turbine power plants and more conventional gas turbine power plants.

## Stages and Gates Methodology

The California Energy Commission utilizes a stages and gates methodology for assessing a project's level of development and for making project management decisions. For research and development projects to be successful they need to address several key activities in a coordinated fashion as they progress through the various stages of development. The activities of the stages and gates process are typically tailored to fit a specific industry and in the case of PIER the activities were tailored to be appropriate for a publicly funded energy research and development program. In total there are seven types of activities that are tracked across eight stages of development as represented in the matrix below.

**Development Stage/Activity Matrix**

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8
Activity 1								
Activity 2								
Activity 3								
Activity 4								
Activity 5								
Activity 6								
Activity 7								

A description the PIER Stages and Gates approach may be found under "Active Award Document Resources" at: <http://www.energy.ca.gov/research/innovations> and are summarized here.

As the matrix implies, as a project progresses through the stages of development, the work activities associated with each stage needs to be advanced in a coordinated fashion. The EISG program primarily targets projects that seek to complete Stage 3 activities with the highest priority given to establishing technical feasibility. Shaded cells in the matrix above require no activity, assuming prior stage activity has been completed. The development stages and development activities are identified below.

<b>Development Stages:</b>	<b>Development Activities:</b>
Stage 1: Idea Generation & Work Statement Development	Activity 1: Marketing / Connection to Market
Stage 2: Technical and Market Analysis	Activity 2: Engineering / Technical
Stage 3: Research & Bench Scale Testing	Activity 3: Legal / Contractual
Stage 4: Technology Development and Field Experiments	Activity 4: Environmental, Safety, and Other Risk Assessments / Quality Plans
Stage 5: Product Development and Field Testing	Activity 5: Strategic Planning / PIER Fit - Critical Path Analysis
Stage 6: Demonstration and Full-Scale Testing	Activity 6: Production Readiness / Commercialization
Stage 7: Market Transformation	Activity 7: Public Benefits / Cost
Stage 8: Commercialization	



## Independent Assessment

For the research under evaluation, the Program Administrator assessed the level of development for each activity tracked by the Stages and Gates methodology. This assessment is summarized in the Development Assessment Matrix below. Shaded bars are used to represent the assessed level of development for each activity as related to the development stages. Our assessment is based entirely on the information provided in the course of this project, and the final report. Hence it is only accurate to the extent that all current and past work related to the development activities are reported.

**Development Assessment Matrix**

Stages Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Develop- ment	5 Product Develop- ment	6 Demon- stration	7 Market Transfor- mation	8 Commer- cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production. Readiness/								
Public Benefits/ Cost								

The Program Administrator's assessment was based on the following supporting details:

### Marketing/Connection to the Market

The researcher has a market connection to Solar Turbines, Inc. in San Diego, California. Solar Turbines supplied information to the researcher during the execution of the grant, and would have aided in the testing of the prototype reactor at pressures higher than atmospheric. Continued connections with gas turbine and fuel cell companies will be required to take the catalytic combustion/fuel reforming device to market.

### Engineering/Technical

Due to technical challenges that consumed more time and funds than expected, the researcher was unable to build and test a prototype reactor to demonstrate the integral catalytic combustion/fuel reforming device at pressures higher than atmospheric pressure. Additional testing is needed at gas turbine operating pressures to understand and optimize the operating parameters for the process. The Program Administrator recommends that the prototype reactor be built and tested.

### Legal/Contractual

The researcher gave no evidence that he has applied for patents or taken any other actions to protect intellectual property.

### **Environmental, Safety, Risk Assessments/ Quality Plans**

Before the selected system can become a product the researcher must prepare quality plans. These include Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety and Environmental.

### **Strategic**

This product has no known critical dependencies on other projects under development by PIER or elsewhere

### **Production Readiness/Commercialization**

The researcher has provided no evidence that he is has prepared a production readiness plan or a commercialization plan. Nor has he provided evidence that he is working with another organization to provide such plans.

### **Public Benefits**

Public benefits derived from PIER research and development are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system.
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply. When the integral catalytic combustion/fuel reforming device becomes a product, it could lead to significantly cleaner gas turbine engine generators, especially those designed for the distributed generation market. The integral catalytic combustion/fuel reforming device could also allow fuel cells to increase system efficiency and better utilize the methane by consuming the anode off-gasses in the catalytic combustion side of this device.

### **Program Administrator Assessment**

After taking into consideration: (a) research findings in the grant project, (b) overall development status as determined by stages and gates, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for follow-on funding within the PIER program.

Receiving follow on funding ultimately depends upon: (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)

# **ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM**

## **EISG FINAL REPORT**

### **INTEGRAL CATALYTIC COMBUSTION/FUEL REFORMING FOR GAS TURBINE CYCLES**

#### **EISG AWARDEE**

University of Maryland  
Dept. of Mechanical Engineering  
College Park, MD  
Phone: (301) 405-2368  
Email: [gsjackso@eng.umd.edu](mailto:gsjackso@eng.umd.edu)

#### **AUTHORS**

Prof. Greg S. Jackson, Principal Investigator

Grant # 99-21

Grant Funding \$74,992

Term: July 1, 2000 – November 31, 2002

PIER Subject Area: Environmentally Preferred Advanced Generation

## **Legal Notice**

This report was prepared as a result of work sponsored by the California Energy Commission (Commission). It does not necessarily represent the views of the Commission, its employees, or the State of California. The Commission, the State of California, its employees, contractors, and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the use of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the Commission nor has the Commission passed upon the accuracy or adequacy of the information in this report.

Inquiries related to the final report should be directed to the Awardee (see contact information on cover page) or the EISG Program Administrator at (619) 594-1049 or email [eisgp@energy.state.ca.us](mailto:eisgp@energy.state.ca.us).

## **Acknowledgement Page**

The author would like to acknowledgement the helpful discussion and collaborations with the following individuals with regards to this project:

Prof. Robert W. Dibble, Univ. of California – Berkeley, CA

Dr. Ken Smith, Solar Turbines, San Diego, CA

Dr. John C.Y. Lee, Solar Turbines, San Diego, CA

## Table of Contents

Abstract.....	1
Executive Summary.....	2
Introduction.....	4
Project Objectives.....	8
Project Approach.....	9
Project Outcome.....	14
Conclusions.....	23
Recommendations.....	24
Public Benefits to California.....	25
Development Stage Assessment.....	25
References.....	25

## List of Figures

<b>Figure 1</b> – Schematics of proposed integral reformer/combustor configurations.....	5
<b>Figure 2</b> – Illustration of catalytic reactions and heat transfer in the integral reactor.....	7
<b>Figure 3</b> – Photographs of flat plate reactor and experimental rig for reactor tests.....	10
<b>Figure 4</b> – Microreactor results for evaluation of Rh-based catalysts for steam reforming.....	13
<b>Figure 5</b> – Samples of flat plate reactor experimental results for integral H <sub>2</sub> catalytic combustion with CH <sub>4</sub> steam reforming.....	17
<b>Figure 6</b> -- Reforming fuel conversion and H <sub>2</sub> selectivity for experimental conditions with $\phi = 0.3$ and $\phi = 0.4$ and $T_{in}$ from 525 to 575°C.....	18
<b>Figure 7</b> – Influence of S/C ratio on experimentally observed reforming fuel conversion and H <sub>2</sub> selectivity for $\phi = 0.3$ and $\phi = 0.4$ and $T_{in}$ from 525 to 575°C.....	19
<b>Figure 8</b> – Comparison of experimental results with numerical model predictions for reforming CH <sub>4</sub> conversion and H <sub>2</sub> selectivity. ....	19
<b>Figure 9</b> – Model profiles comparing reactor temperatures, reforming CH <sub>4</sub> conversion, and combustion H <sub>2</sub> conversion at 1 atm and 4 atm.....	21
<b>Figure 10</b> – Model results showing increased conversion (relative to Figure 9a with reduced velocities on both sides of the reactor.....	22

## Abstract

A combined experimental and numerical investigation was undertaken to assess the stability of integral catalytic combustion / reforming of CH<sub>4</sub> for producing H<sub>2</sub> for gas turbine or fuel cell power cycles. Results indicate that integration of catalytic combustion with steam reforming in alternating flow channels is constrained by the high-temperature activation for CH<sub>4</sub> catalytic combustion and steam reforming and by temperature limits to maintain reliable long-term catalyst performance. Along with CH<sub>4</sub>, H<sub>2</sub> was studied as a combustion fuel in the integral reactor configuration because of its availability in solid oxide fuel cell anode exhaust. Several support and catalyst combinations in flat plate reactor experiments were investigated for CH<sub>4</sub>-steam reforming with CH<sub>4</sub> and H<sub>2</sub> as the combustion fuel. A  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported rhodium catalyst for reforming with a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported palladium catalyst for combustion was finally selected due to the activity at intermediate temperatures (500°C < T < 700°C) and catalyst stability at high temperatures (T > 700°C). Experimental and numerical results with H<sub>2</sub> as the combustion fuel – relevant for solid oxide fuel cell systems – indicated that a stable reactor configuration could be designed with relatively low inlet temperatures. Stability for a reactor with CH<sub>4</sub> combustion requires high reactor inlet temperatures that may be attainable through thermal integration within a gas-turbine combustion system. Although the project has not demonstrated a full-scale reactor, this study provides unique experimental and numerical support for optimizing catalytic combustion and steam reforming for volumetrically efficient and ultra-low NO<sub>x</sub> production of H<sub>2</sub> from natural gas.

*Keywords:* Catalytic combustion, steam reforming, hydrogen production, gas turbines, solid oxide fuel cells



## Executive Summary

This project established the basis for future development of an integral catalytic combustor / steam reformer for producing H<sub>2</sub>-rich reformat from natural gas for next generation power plant applications such as stabilization of ultra-low NO<sub>x</sub> gas turbine combustors or pre-reforming in solid oxide fuel cell power plants. The integral catalytic combustor / steam reformer provides removal of heat directly from the combustion process through solid-phase conduction heat transfer from the combustion catalyst to the reforming channels. This reactor design allows for combustion at high equivalence ratios and for very high heat transfer rates to the reforming catalysts for stable reforming at temperatures below 800°C, where conventional steam reformers operate. The technology development in the current project involved evaluation of combustion / reforming catalyst combinations in a flat-plate reactor at atmospheric pressure to assess reactor operability.

These tests were also used to validate numerical models with detailed chemistry to establish the basis for reactor design and performance at high pressure conditions expected in actual applications. The original project objectives had included the development of a prototype reactor from these initial efforts, but challenges in identifying stable catalyst combinations in the flat-plate reactor tests delayed the project and did not permit this final phase. Nonetheless, the project results provide a solid basis on which to design and test the prototype reactor for eventual commercial development for ultra-low emissions combustion systems and future fuel cell power plant applications. The development objectives of the project as listed here provided outline the project approach to addressing possible challenges to implementing integral catalytic combustion / steam reforming:

- 1) identify preferred reliable supported catalyst combinations,
- 2) test selected catalyst combination in flat-plate reactor to assess reactor performance,
- 3) develop models for integral catalytic combustor / reformer design and operability,
- 4) assemble and test sub-scale prototype of integral reactor at high pressure conditions,
- 5) analyze reactor performance in advanced fuel cell / gas turbine cycles.

Due to the lack of high-pressure testing as originally planned, the focus of the project was principally the assessment of preferred catalysts, design approaches, and reactor operability through the flat-plate reactor tests and through numerical models validated with the flat-plate reactor data. The flat-plate reactor tests and modeling provided a simplified geometry for providing valuable catalyst performance and heat transfer modeling to determine the necessary features of a full-scale reactor design.

The flat-plate reactor tests and numerical modeling identified the need for high activity reforming catalysts, i.e. rhodium-based supported catalysts, to minimize the risk for thermal runaway of the catalytic combustion process. The high activity Rh-based reforming catalysts provided adequate rates for endothermic steam reforming on one side of the reactor wall to permit catalytic combustion at relatively high fuel/air ratios which would otherwise result in over-temperature on the catalyst surface. Other significant outcomes from the project included: the observation of enhanced reactor operability and low-temperature performance with H<sub>2</sub>

combustion in comparison to CH<sub>4</sub> combustion over the preferred Pd-based combustion catalysts, intermediate temperature operation (between 600 and 750°C) with Rh reforming catalyst, and the establishment of the important operating parameters under high pressure conditions through the implementation of detailed numerical models.

Numerous experiments results with H<sub>2</sub> catalytic combustion as the heat source indicate that the integral reactor is well suited for burning fuel cell anode exhaust in fuel cell / gas turbine cycles. Furthermore, Rh-based reforming catalysts provide the necessary activity to sustain high conversion of CH<sub>4</sub> to H<sub>2</sub> at temperatures < 800°C and thereby to control combustion catalyst temperatures. This result establishes the potential for the integral reactor for sustaining catalytic combustion at low temperatures and for providing good volumetric efficiency for H<sub>2</sub> production. For gas turbine applications, experimental results suggest that the use of an integral reactor to convert a fraction of a CH<sub>4</sub> fuel stream to H<sub>2</sub>/CO would require higher temperature combustion catalysts less prone to deactivation than conventional Pd-based catalysts, but with less low-temperature activity necessary for reactor start-up. Either way, the flat-plate reactor experiments and the associated numerical models identified the importance of moles of combustion fuel to moles of reforming fuel in establishing reliable steady-state reactor performance within catalyst temperature limits. The results also indicate that the best reactor design would involve a co-flow system where the high combustion and reforming rates occur near the entrance to the reactor.

Development of the proposed integral catalytic combustor / steam reformer for natural gas is not completed, but the project results and the design tools developed in this project provide the basis for completion. The experimental and numerical results establish the reactor as a valuable approach for burning fuel cell exhaust to make additional H<sub>2</sub> for fuel cell operation. Based on the outcomes from this preliminary evaluation of this reactor concept, recommendations for further development are briefly summarized here:

- 1) Demonstrate a prototype reactor at pressures of 5 atm or higher.
- 2) Investigate possibility of using new Pd-doped hexa-aluminate catalysts for operating temperatures > 900°C with CH<sub>4</sub> as the combustion fuel.
- 3) Test for durability of preferred catalyst combinations at cycle operating conditions.
- 4) Develop a reactor operation strategy for fuel cell / gas turbine power plants and more conventional gas turbine power plants.

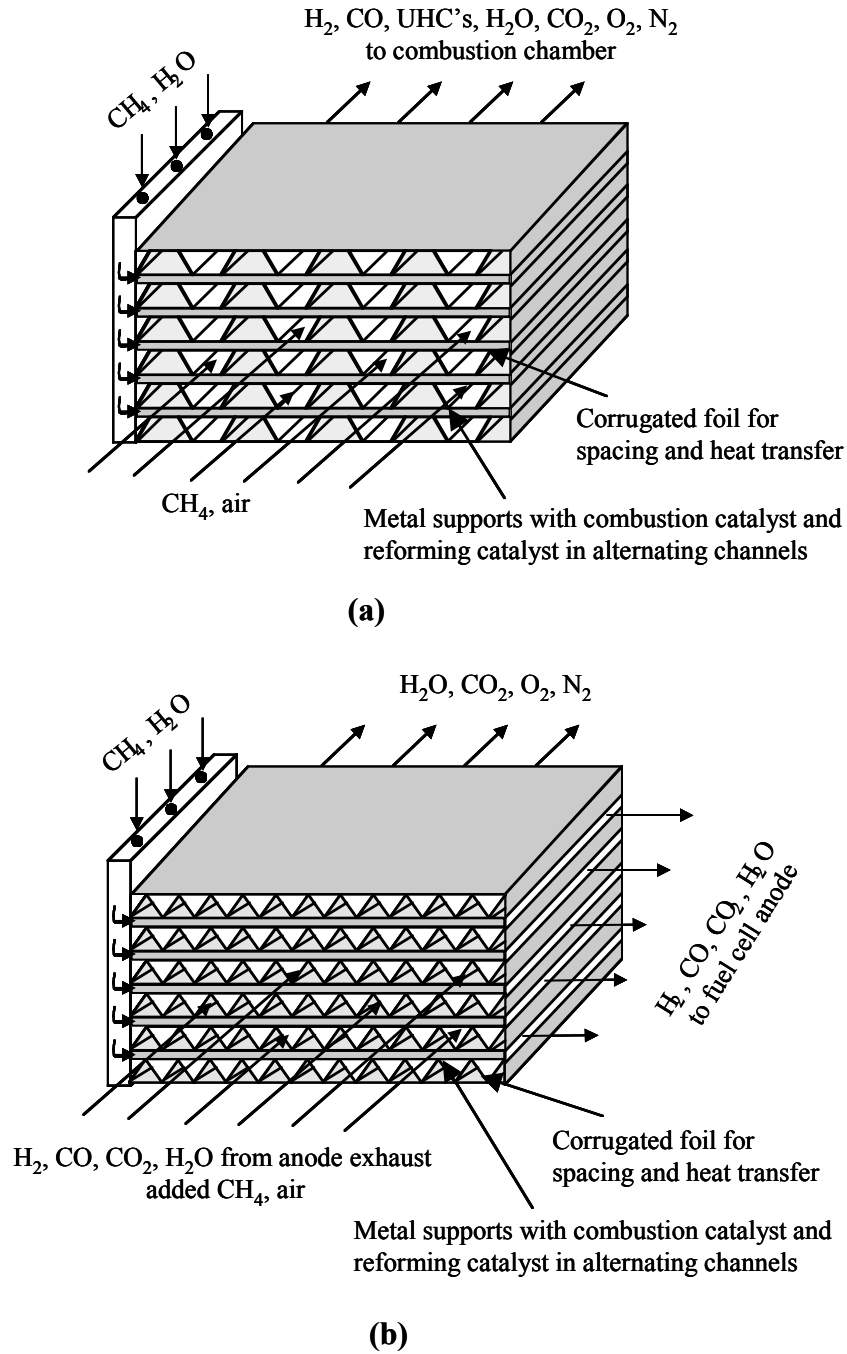
The ultimate success of this project in demonstrating operability of an integral reactor with stable catalyst temperatures for gas turbines with ultra-low emissions will provide a unique approach for gas turbines within California to meet BACT standards. Successful development of the proposed integral catalytic combustor / steam reformer for natural gas will also provide technical expertise within the state for the emerging areas of solid oxide and molten carbonate fuel cell power plants. While it is difficult to quantify the future market for high temperature fuel cells, it is clear that ultra-clean power generation is currently headed in the direction of fuel cells. The development of the integral reactor concept will provide critical enabling technology within the state for the realization of these power plants of the future.

## Introduction

The requirement of ultra-low emissions for stationary power plants in California, Japan and more recently other U.S. regions has been a large driving force in the development of ultra-lean premixed combustion systems [1] and solid-oxide fuel cells [2] that run on natural gas. In the case of both of these power plants, the benefits of incorporating an efficient reactor for converting  $\text{CH}_4$  to  $\text{H}_2/\text{CO}/\text{CO}_2$  can be substantial. In the case of lean-premixed combustion systems,  $\text{H}_2$  addition to natural gas-fueled combustion systems has been shown to be an effective means of providing gas turbine combustor stability at conditions where  $\text{NO}_x$  emissions are well below 10 ppm [3,4]. For solid oxide fuel cells, although much research has been performed on internal reforming or direct electrochemical oxidation of  $\text{CH}_4$ , improved reliability and more efficient fuel cell performance can be attained with some external pre-reforming (i.e.,  $\text{H}_2$  production in a separate reactor) [5,6]. Thus, the development of volumetrically efficient reactors for conversion of  $\text{CH}_4$  to  $\text{H}_2/\text{CO}$  reformat has received a lot of attention both for improving stability in lean-premixed combustion systems [3,7] and even more so for improving performance in high temperature fuel cell applications [8-10]. The current project investigated the integration of  $\text{CH}_4$  steam reforming with catalytic combustion in a reactor configuration with alternating reforming and combustion pathways. This project funded under the “Environmentally Preferred Advanced Generation” category of the Public Interest Energy Research Program of the California Energy Commission focused on the development of and operability limits for such integral catalytic reformer/combustors.

The integration of catalytic combustion with endothermic steam reforming for  $\text{H}_2$  production has been proposed and investigated for some applications [11,12]. However, previous studies have generally provided simple proof of concept demonstrations and minimal development without addressing the complexity in designing and operating a combined combustor/reformer, particularly for natural gas applications. The project discussed here focused on the reactor performance and operability for two applications for producing  $\text{H}_2/\text{CO}$  reformat. The two applications illustrated in schematics in figure 1a) – where reformat is used to stabilize ultra-low  $\text{NO}_x$  combustion in a downstream burnout zone, and in figure 1b) – where the reformat provides the fuel for a fuel cell anode. This study explores the challenges to achieving the potential advantages/benefits of the integral reactor configuration. For example, the proposed thermal integration of endothermic steam reforming of  $\text{CH}_4$  can provide temperature control for the catalytic combustion channels and thereby reduce premixing requirements and autoignition risks for the combustion flow path. Furthermore, the removal of heat directly from the combustion process through the surface heat transfer to the reforming channels allows for combustion at higher equivalence ratios ( $\phi_{\text{comb}}$ ) without excessive reactor temperatures and associated  $\text{NO}_x$  production. The increased  $\phi_{\text{comb}}$  also reduces airflow requirements for burning.

The advantages of integrating endothermic reforming with catalytic combustion require careful reactor design and catalyst selection such that local surface temperatures within the reactor can be maintained within the limits of low-temperature catalyst activity and high-temperature catalyst stability. Various approaches have been considered for avoiding over-temperature in catalytic combustion systems for high-firing temperature gas turbines. Such approaches include the use of Pd/PdO transitions for reducing high temperature catalyst activity [13,14] and selectively-coated reactors for limiting surface reactions [14,15]. The transition of



**Figure 1** – Schematics of proposed integral reformer/combustor configurations: a) configuration for burning  $\text{CH}_4$  in a combustor to provide  $\text{H}_2$  for ultra-lean flame stabilization and b) configuration for burning fuel cell anode exhaust and additional  $\text{CH}_4$  for providing reformat to fuel cell anode.

Pd-based catalysts from an oxidized to a reduced state at intermediate temperatures has been shown to reduce combustion activity above 800 to 900°C under some conditions [16]. However, at conditions with high O<sub>2</sub> partial pressures (as in gas turbine combustor inlets), the reduced Pd remains active as a combustion catalyst and is not always effective at avoiding catalyst overheating [17] on its own merits. The limits of Pd-based catalysts for controlling combustion temperature have led to recent developments of reactors with partial coatings, which provide internal cooling to avoid high reactor surface temperatures during combustion. Integrating endothermic steam reforming with the catalytic combustor can provide the potential for mitigating the risk of overheating (i.e. above 1000°C for Pd-based catalysts [17]) in the combustion channels and at the same time permit operation of higher  $\phi_{\text{comb}}$  (or similarly less stringent fuel/air premixing) than in more conventional catalytic combustor configurations. Successful demonstration of the proposed integral reactor thus can provide not only a volumetrically efficient approach to H<sub>2</sub> production from CH<sub>4</sub>, but also an alternative approach for ultra-low emissions catalytic combustors for new high-firing temperature gas turbines.

Recent advances in combining molten-carbonate and solid-oxide fuel cells [18] with small gas turbines have laid the foundation for ultra-clean (< 3 ppm NO<sub>x</sub>) and extremely efficient power generation ( $\eta_T > 60\%$ ) starting with natural gas as the fuel. These cycles can benefit from the incorporation of a burner of the fuel cell anode exhaust (which consists predominantly of oxidation products H<sub>2</sub>O and CO<sub>2</sub> with residual H<sub>2</sub> and CO fuel for combustion) [5,6,19]. In many of these cycles, there is a clear opportunity for catalytic combustion technology to provide a means of stable combustion for the endothermic reforming process without a significant NO<sub>x</sub> penalty. With combustion in the integral reactor, combustion emissions are achieved while simultaneously providing the necessary high temperatures and heat fluxes for steam reforming to provide adequate CH<sub>4</sub> conversion and to avoid surface carbon buildup over typical reforming catalysts (such as nickel [20] or rhodium [21]). However, these benefits are bracketed by low-temperature limitations on the catalyst activity and high-temperature limits on the catalyst stability for both combustion and CH<sub>4</sub> reforming. The catalytic combustion stability is greatly enhanced in fuel cell applications where fuel cell anode exhaust with readily active H<sub>2</sub> and CO are available for the combustion channels, but the challenges to maintain high reforming conversion depends on controlling the integral reactor operating temperatures such that the combustion and reforming catalysts maintain adequate activity and stability. The current project explored these limitations and developed experimental and numerical tools to assess the feasibility of maintaining steady-state conversion and providing reliable transient start-up operation for the integral catalytic reformer/combustor.

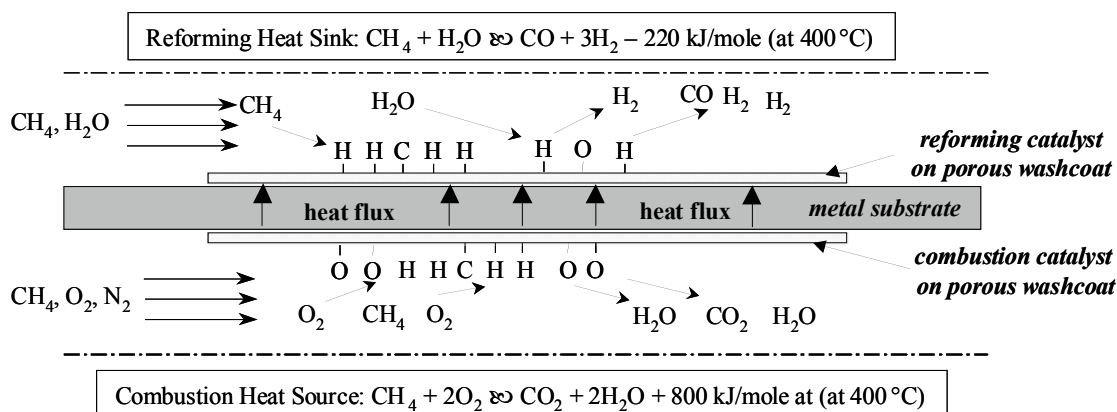
This initial project was established to perform an evaluation of catalyst combinations and to perform bench scale testing of these combinations in a simple flat-plate reactor with a down-select leading to bench-scale reactor tests under full operating conditions. The final goal of the project was to establish the collaboration with a partner (Solar Turbines in San Diego, CA) to demonstrate the reactor in field experiments for combustion stabilization. Thus, according to the Energy commissions stages and gates project, the project was designed to reach a “Stage 4” level of technology development with preparations for field experiments. However, due to challenges in identifying stable catalyst combinations in initial flat-plate reactor tests, the program was delayed in achieving its full objectives and thus the project completed most of the “Stage 3” level of development with completed research and bench scale testing. The project does however

continue with efforts at Solar Turbines to develop the integral reformer/combustor concept for advanced gas turbine combustor designs for ultra-low emissions ( $< 5$  ppm  $\text{NO}_x$ ). This initial project here provides Solar and other possible technology developers with essential design and catalyst evaluation necessary for developing a successful integral catalytic reformer/combustor. The details of this initial experimental and numerical analysis as the basis for complete technology development are discussed fully in the subsequent sections.

This project report lays out the accomplishments of this study. The proceeding section first lays out the project objectives and the principals underlying the proposed concept lays. The subsequent section focuses on accomplishments in the program and to what extent these outcomes met the original program objectives. Finally, conclusions are drawn about the design of an integrated steam reformer / catalytic combustion system, and recommendations are made as to where further development and applications should be pursued for this technology based on the results of this study. The benefits of this study to developers in the state of California are also briefly discussed.

## Project Objectives

The project was originally proposed to develop and demonstrate critical design features necessary for integrating endothermic catalytic steam reforming, which is generally driven by inefficient indirect gas-to-surface heat transfer, with exothermic catalytic combustion, which is prone to thermal “runaway” (or reactor overheating). By utilizing direct heat transfer across thin metal plates that separate reforming and combustion channels, the integral reactor has the potential with careful design and catalyst selection of providing extremely good temperature control both for volumetrically-efficient  $\text{H}_2$  production and for ultra-low  $\text{NO}_x$  combustion of a fuel stream. The heat transfer for the control of temperature in the integral reactor is illustrated in the schematic in Figure 2, which shows a small section within the reactor where  $\text{CH}_4$  catalytic combustion and steam reforming are occurring on opposite sides of the reactor substrate.



**Figure 2** – Illustration of catalytic reactions and heat transfer in the integral reactor where  $\text{CH}_4$  combustion is used to drive endothermic  $\text{CH}_4$  steam reforming for volumetrically efficient  $\text{H}_2$  production.

There have been a few published demonstrations of integral catalytic combustor/reformers in Europe [11,12], which have shown the effectiveness of the integration in controlling reactor temperatures. Similar reactors are now being developed for low-temperature H<sub>2</sub> production with alcohols for fuel cell applications within some fuel cell system integration companies [22]. The current program, however, has been distinct from those previous efforts in its attempt to develop design principles through initial fundamental studies using simplified reactor configurations and validated numerical models. The program objectives were thus strictly technical leading up to a “Stage 4” prototype demonstration after a broad-based “Stage 3” study to develop critical guidelines for design of integral combustion / steam reforming systems.

The original objectives of the program are laid out in the original proposal narrative. Those objectives as listed here provided the basis for the original work plan:

- 1) identify preferred reliable supported catalyst combinations for integral combustion and steam reforming with metallic reactor substrates,
- 2) test selected catalyst combination in flat-plate reactor to identify steady-state and transient performance of reactor,
- 3) develop models for integral catalytic combustor / reformer design and assessment of performance potential at conditions expected in actual applications,
- 6) assemble and test sub-scale prototype of integral reactor and demonstration at high pressure conditions,
- 7) analyze reactor performance in advanced cycles with fuel cell / gas turbine combinations.

The project achieved the first three objectives successfully with completion of the work at the University of Maryland. Thus, the objectives up to “Stage 3” development were largely completed. Unexpected challenges in meeting the first three objectives delayed the project and resulted in budgetary and time constraints, which did not permit the completion of the fourth “Stage 4” objective. In spite of these shortcomings, development efforts for an integral catalytic combustor / reformer are continuing with efforts ongoing at Solar Turbines in consultation with the University of Maryland. Due to the lack of high-pressure testing, which would have been completed in the prototype reactor tests, it was difficult to assess the reactor performance in advanced cycles under high-pressure conditions. Nonetheless, some model results from results obtained in meeting the third objective were used to evaluate how the reactor might be expected to perform and impact a hybrid gas turbine / fuel cell power plant [5,6,18,19]. Thus, the selected completion of the first three project objectives provides commercial developers with critical results as well as available modeling tools for developing integral catalytic combustion / steam reforming systems for future generation power plants utilizing gas turbines and/or high-temperature fuel cells.

## **Project Approach**

The integral catalytic combustor / steam reformer project involved several phases which would provide critical reactor design information and in the original plan lead to a prototype

demonstration. The specific tasks, which were completed under the project, outline the approach taken to achieve the project objectives:

- 1) Screening of catalysts and supports in micro-reactor configurations,
- 2) Testing of catalytic coating combinations in flat-plate reactor,
- 3) Development of reactor models for reactor design and prototype development,
- 4) Analysis of reactor effectiveness in advanced gas turbine / fuel cell cycles.

The initial two tasks assessed the performance of different catalyst / support combinations as catalytic washcoats for both combustion and steam reforming. It was critical to develop catalytic coatings that provide good adhesion to metal substrates because metal substrates were needed to provide thermal conductivity and workability at acceptable costs for a feasible reactor design. The testing of combustion / steam reforming catalysts on the opposite sides of a flat-plate metal substrate were then used to determine the compatibility of different combination of combustion / reforming catalysts. These tests furthermore provided the basis for evaluating operability ranges for the reactor at least under atmospheric pressure conditions and further for validating catalytic chemistry mechanisms that were incorporated into reactor models for predicting the functionality of fuel conversion,  $H_2$  selectivity, and reactor temperatures for a much broader range of operating conditions. These model results provide a basis for the reactor design and combined with the preliminary analysis of reactor integration in advanced gas turbine / fuel cell cycles provides a basis for continued reactor development for actual commercial applications.

Brief descriptions of the approaches taken in each of the four completed tasks are presented here:

#### *Task 1: Screening of catalysts and supports in microreactor*

Although there has been substantial work on optimizing catalysts for  $CH_4$  combustion and  $CH_4$  steam reforming, the proposed integral reactor presents unique conditions for both catalytic combustion and steam reforming. The need for low-temperature activity for rapid ignition and for compatible activities on both the combustion and reforming channels established a basis for a preliminary screening of supported catalysts for both the combustion and reforming sides of the reactor. Catalysts were screened in a microreactor configuration, which has been described in detail elsewhere [23]. The microreactor consists of an annular flow path with a washcoat-supported catalyst on the outer surface of the inner tube. Various combustion and reforming catalysts were tested on their own to assess low-temperature activity and high steady-state conversion. Conversion and product selectivity were measured by using a quadrupole mass spectrometer (VG GasLab 300) for residual gas analysis. For the reforming tests, an Argon diluent replaced  $N_2$  to permit measurement of CO in the exhaust stream by the mass spec. Ar was bubbled through a saturator at a controlled temperature to provide steam for the microreactor steam reforming tests.

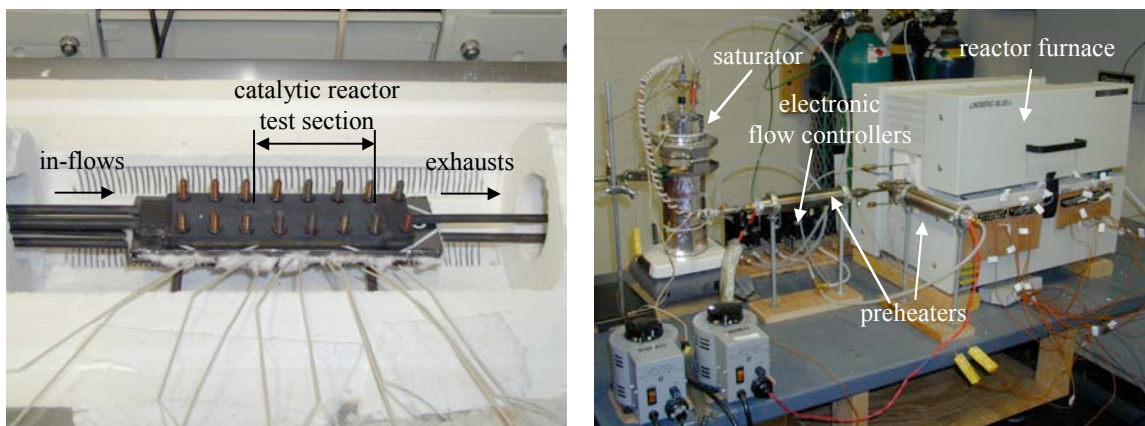
All supported catalysts were prepared by an incipient wetness technique described elsewhere [23]. For the combustion catalysts, the requirement for low-temperature  $CH_4$  activity limited the selection to Pd-based catalysts [24]. After testing different supports with pure Pd-catalysts, it was determined that conventional  $\gamma-Al_2O_3$  washcoats with their high surface area still provided the best low-temperature activity. For the reforming catalyst, various Ni-based and Rh-based supported catalysts were tested. Although Ni-based catalysts are typically preferred for their cost



effectiveness, the improved durability and activity at lower temperatures of the Rh-based catalyst made it a preferred for the integral reactor tests. The Rh-based catalysts were tested with a variety of oxide supports, and it was found that  $\gamma\text{-Al}_2\text{O}_3$  again provided the best combination of low-temperature activity and steady-state conversion in microreactor tests. The  $\gamma\text{-Al}_2\text{O}_3$  washcoats are known to form aluminates and to undergo surface reduction loss at temperatures above  $1000^\circ\text{C}$ . However, because the integral reactor configuration is specifically designed to maintain surface temperatures within a narrow window that can remain below  $1000^\circ\text{C}$ , these high-temperature shortcomings of  $\gamma\text{-Al}_2\text{O}_3$  can be avoided.

*Task 2: Testing of catalytic coating combinations in flat-plate reactor*

The principal reactor configuration tested in this project was designed to provide results that could be interpreted for general reactor design. To this end, experiments with a flat plate reactor were carried out. The flat plate reactor substrate consisted of an oxidized Fecralloy plate with selected catalytic coatings from Task 1 deposited on opposite sides of the plate in a 5.5 cm long X 2.0 cm wide reactor test section. The pre-oxidized Fecralloy provided a rough  $\text{Al}_2\text{O}_3$  rich surface to which the  $\gamma\text{-Al}_2\text{O}_3$  washcoats adhered without spalling. The Fecralloy plate was placed within a reactor housing such that two independent flow paths were established on opposite sides of the plate: one side for catalytic combustion and the opposing side for catalytic steam reforming of  $\text{CH}_4$ . The flows through the reactor were arranged in a co-flow configuration because it was ascertained from modeling that co-flow would provide the best match for balancing the heat release from the combustion with thermal energy removal by the endothermic reforming. The reactor was instrumented with very thin (0.12 mm diameter wire) K-type thermocouples, which were carefully spot-welded along the plate to minimize flow disturbances as well as loss of catalyst activity. Fig. 3a shows a photograph of the instrumented reactor indicating the location of the catalytic test section. The reactor operated inside a furnace, which was kept at a temperature near the desired reactant inlet temperatures to approximate adiabatic reactor operation as might be expected in a larger prototype reactor.



**Figure 3** – a) Photograph of flat plate reactor with thermocouples inside furnace for testing simultaneous catalytic combustion / steam reforming. b) Photograph of experimental rig for flat plate reactor tests including saturator for steam injection and flow preheaters (control computer and mass spec for residual gas analysis not shown).

The combustion and reforming flows into the reactor were preheated outside of the reactor and controlled via a computer and electronic mass flow controllers. For the combustion side the fuel and air are premixed just upstream of the catalyst test section in a quartz wool mixer. This premixing just before the catalyst was required particularly for tests using  $H_2$  as the combustion fuel due to the high probability of  $H_2$  autoignition before the combustion catalyst. The oxidizer and combustion diluent (either  $N_2$  or Ar) were preheated outside the furnace to a desired temperature. For the reforming flow, the diluent (always Ar) was passed through a bubbler with at a controlled temperature to pick up steam, which was then passed into a preheater before being mixed with  $CH_4$  upstream of the flat-plate reactor. Most components of the experimental test facility are illustrated in the rig photograph shown in fig. 3b.

The VG GasLab 300 mass spectrometer was used in these tests for exhaust gas analysis of the reforming stream. The exhaust gas analysis provided transient  $CH_4$  conversion and  $H_2$  selectivity for the reforming half of the reactor. The temperature profile was used to simultaneously assess fuel conversion on the catalytic combustion side of the plate reactor.

Numerous tests were performed to find stable operating conditions and optimal  $H_2$  production in the flat plate reactor with different selected catalyst combinations, reactor inlet temperatures, combustion fuels ( $CH_4$  or  $H_2$ ), combustion equivalence ratio ( $\phi$ ), and reforming steam to carbon ratios (S/C). These results provided the basis for assessing the operability of a given catalyst combination in a larger reactor. These results also provided a means for validating a flat-plate reactor numerical model for integral catalytic combustion / steam reforming. This numerical model discussed in the following sub-section was the link between these flat plate tests and reactor design and overall performance assessment.

### *Task 3: Development of reactor models for reactor design*

The flat-plate reactor tests provided an assessment for the range of inlet conditions (temperatures, velocities, and flow composition) of the two independent streams that provided reliable reactor performance at atmospheric pressure. The flat-plate reactor was not designed to achieve full conversion of the fuel streams, but rather to give less than full conversion such that valuable kinetic information was obtained for validating a reactor model, which could then be used for reactor design of a prototype system. The design aspects evaluated by the model include reactor length and flow velocities, channel heights, catalytic washcoat loadings, and inlet conditions. Furthermore, the model, as described in the following paragraphs, provides a basis for assessing how high-pressure conditions (4 atm. or more) may impact the performance of the integral catalytic combustor / steam reformer.

The numerical model of the integral catalytic combustor / steam reformer developed for this project (and which is available for commercial developers) was adapted from single channel reactor models [25] for investigating transient behavior of catalytic combustors with washcoat-supported catalysts. The integral catalytic combustor / steam reformer model combines two single channel models with multi-step surface chemistry models and a finite volume heat transfer model for the separating substrate wall to evaluate transient behavior of the integrated processes. To integrate over time scales of several minutes or longer in a computationally efficient manner, a quasi-1-D formulation was implemented where local heat and mass transfer correlations were used to determine the differences in temperatures and species concentration between each

channel flow and the respective porous washcoats. Details of the model are presented elsewhere [26] and only a brief discussion of critical aspects is provided here.

Two aspects of the numerical model were critical for predicting reactor performance: 1) transport of heat and mass from the channel flow to the catalytic washcoats, and 2) surface and gas-phase chemistry mechanisms for catalytic and homogeneous conversion of fuel to products. For heat and mass transport from the channel flow to the catalytic washcoat, the model used a modified Graetz number heat and mass transfer correlations for reacting laminar flow based on a previous study [27]. Use of these correlations allowed for the calculation of temperature and species concentrations at the washcoat/channel flow interface and these conditions were used in a porous catalytic washcoat sub-model with detailed surface chemistry to predict catalytic reaction rates in both the reforming and combustion channels. For the surface chemistry mechanisms, only a limited number of surface chemistry models for specific catalyst compositions are available for both CH<sub>4</sub> catalytic combustion and steam reforming. Fortunately, some preliminary detailed surface chemistry models have been developed for catalytic combustion of CH<sub>4</sub> and H<sub>2</sub> over Pd-based catalysts [23,25], for partial oxidation of CH<sub>4</sub> over Pt [28] and Rh [28,29], and for steam-reforming of CH<sub>4</sub> over Ni [30] catalysts. Modeling results, as discussed in the project outcomes and in additional references [25], were obtained using the Pd combustion mechanism and a modified version of the Rh partial oxidation mechanism [29] such that it incorporated steam-reforming reactions. Although other results were obtained for the integral reactor with the Ni steam reforming mechanism, the poor activity of the Ni-based catalysts for the high reactor space velocities resulted in poor performance of the Ni-based catalyst in the reactor which did not agree well with the model predictions. Thus, the modeling results for the Rh-based reforming catalyst are reported in this final report and the implications of these modeling results for further development of the integral reactor are discussed in the following sections.

#### *Task 4: Analysis of reactor effectiveness in advanced cycles*

With the original project plan, the final objective involved an assessment of the reactor performance in advanced gas turbine / fuel cell cycles. Such analysis can only be fully done with some assessment of critical reactor performance under high-pressure conditions where things such as pressure drop, conversion, and reactor heat loss can be measured. Thus, due to the lack of high-pressure testing in this study, analysis of the reactor in advanced power cycles was limited to idealized models which looked at the impact of improved integration of combustion with reforming on the cycle performance. The improved integration permitted a broader range of combustion fuel/air ratios and reduced heat losses out of the system from the combustion system. The effects of these improvements which are expected to be derived from the integral reactor were investigated in a cycle model of a combined solid oxide fuel cell / gas turbine power plant following the design presented in a previous reference [19]. The model used global zero-dimensional sub-models for the reactor, fuel cell, compressors, turbine, and necessary heat exchangers. The equations for the sub-models were solved simultaneously in a non-linear simultaneous equation solver. The sub-model for the integral reformer assumed equilibrium for the converted reactants and the sub-model for the fuel cell used resistances and overpotentials for average fuel cell conditions based on used-specified conversions of the various fuel sources (H<sub>2</sub>, CO, and CH<sub>4</sub>) exiting from the reformer. In general, CH<sub>4</sub> conversion in the solid oxide fuel cell was less than that used for H<sub>2</sub> and CO, which are expected to undergo much more rapid

oxidation in the fuel cell anode. Results for the advanced cycle model are presented in brief in the following section.

## Project Outcomes

Although the project did not attain all of its original objectives due to the extended time for identifying preferred reforming catalysts and operating conditions from the flat-plate reactor studies, the project did achieve success in some of the initial Stage 3 development objectives. To that end, the project identified the need for high activity reforming catalysts to minimize the risk for thermal runaway of the catalytic combustion process. Furthermore, the flat-plate reactor tests indicated that catalytic combustion at relatively high  $\phi$  is feasible in the integral catalytic combustor / steam reforming reactor and thus less air / O<sub>2</sub> flow is needed for the burner than if a combustor is operated in a stand-alone mode. Although these results need further verification in prototype reactor tests at high pressure, they lay the groundwork for a new approach to H<sub>2</sub> production for gas turbine combustion stabilization and for high temperature fuel cell power plants. The most significant outcomes for this project are thus summarized as follows:

- 1) identification of washcoat supported Rh catalysts for matching activity of Pd-based combustion catalysts,
- 2) demonstration of integral catalytic combustion / steam reforming with Rh-reforming and Pd-combustion catalysts for a range of combustion equivalence ratios with both H<sub>2</sub> and CH<sub>4</sub> as the fuel source,
  - a) observation of enhanced performance with H<sub>2</sub> combustion in comparison to CH<sub>4</sub> combustion
  - b) establishing intermediate temperature operation (between 600 and 750°C) of the integral reactor with Rh reforming catalyst
- 3) development of detailed numerical model for reactor design and initial assessment of reactor performance under high-pressure operating conditions,
- 4) analysis of the impact of integral catalytic combustor / steam reformer for improving advanced cycles combining gas turbines and solid oxide fuel cells.

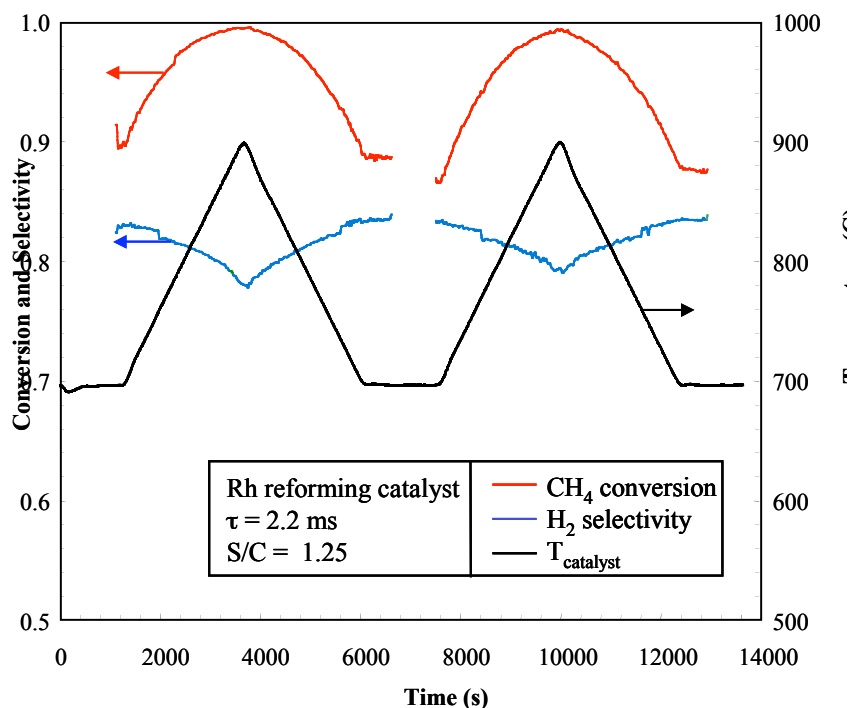
The above summary of the project results highlights the achievements, which were directed toward meeting project objectives 1, 2, 3, and 5 stated in the previous section. Objective 4 was not met due to the failure to establish prototype design criteria in sufficient time. The above accomplishments are further spelled out in the following subsections. Future efforts to still meet the goals of objective 4 are being considered with further collaborations between Solar Turbines and the University of Maryland.

### *Results for Objective 1: Identification of preferred catalytic coatings*

Microreactor studies of various catalytic coatings for both combustion and reforming established the preferred catalysts to be implemented in the flat-plate reactor tests and further to be recommended for prototype integral reactor development. As stated earlier, the design specification for low-temperature CH<sub>4</sub>-combustion activity to sustain fast light-off / reactor start-up implicated the need for Pd-based catalysts for combustion [24]. The alternative use of H<sub>2</sub> as the combustion fuel source, as likely in a fuel cell power plant, may allow for alternative combustion catalysts, but Pd-based catalysts were very effective as low-temperature catalysts for

H<sub>2</sub> combustion even down to 100°C [23]. In comparing different supports Pd-based catalysts supported on high surface area  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoats were shown to be more active than on ZrO<sub>2</sub> supports, and thus Pd on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoats was selected as the combustion catalyst. A broad literature on the challenges associated with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoats and Pd catalysts at high temperatures is well documented [24]. In particular, the concerns of PdO<sub>x</sub>-reduction limiting combustion activity at high temperatures (above 800°C) present a serious challenge. While these concerns are mitigated for the current application by the control of temperature with the back-side reforming reactions, both modeling results and flat plate reactor experiments showed that transient high temperatures conditions can cause a phase change in the PdO<sub>x</sub> catalyst and a subsequent loss in activity for CH<sub>4</sub> oxidation. While the issue of Pd-reduction and loss of activity did arise under some conditions involving higher temperature operation with CH<sub>4</sub> combustion, the issue did not significantly impact H<sub>2</sub> combustion performance due to the increased activity of H<sub>2</sub> on reduced Pd at all temperatures.

While the choice of the combustion catalyst for low temperature activity was rather straightforward, the selection of a compatible reforming catalyst with comparable activity for steam reforming at temperatures ranging from 600°C to 800°C was less obvious. The microreactor studies indicated that the common Ni-based catalysts did not have adequate activity at high reactor space velocities expected for the integral reactor. Although different supports were tested with Ni catalyst, no Ni-supported catalysts tested in the microreactor indicated adequate steam-reforming activity to provide rapid thermal energy extraction from the Pd-based catalytic combustion. Further microreactor tests were then pursued with Rh-based catalysts, which showed almost an order of magnitude increase in steam reforming activity for similar



**Figure 4** – Microreactor results for Rh-based catalyst similar to selected catalyst used in flat-plate reactor tests

loadings vs. the Ni-based catalysts. Results from an example microreactor tests showing CH<sub>4</sub> conversion and H<sub>2</sub> selectivity for steam reforming over a Rh catalyst for a range of temperatures are shown in Figure 4. Figure 4 indicates conversions very near mass-transfer-limited values at temperatures below 800°C for relatively small residence times (< 2.5 ms) over the washcoat-supported catalyst, which suggests that the Rh kinetics are optimal for rapid thermal extraction of combustion heat release through the integral reactor substrate wall. Specification of the Rh-based catalysts for CH<sub>4</sub> steam reforming has been reported in the literature [33] although Ni catalysts have often been preferred due to costs. However, for the integral reactor the higher activity of Rh catalyst will allow for a significant reduction in reactor size and more importantly provides improve thermal control and thus avoidance of high temperature deactivation of Pd-based combustion catalysts.

#### *Results for Objective 2: Flat-plate reactor tests*

Numerous experiments were conducted with the flat plate reactor in order to determine the operability of the integral reactor concept for H<sub>2</sub> production from CH<sub>4</sub> over a range of inlet conditions: including reactor inlet temperature, combustion  $\phi$ , reformer S/C ratio, moles of combustion fuel to moles of reforming fuel, and reactor inlet velocities. The flat plate reactor tests, which consumed the bulk of effort in this program, revealed several unexpected results that gave critical information for further reactor development. Results can be summarized as follows:

- 1) CH<sub>4</sub> combustion on the Pd/ catalysts does not provide the rapid conversion without extremely high loadings of Pd for stable reactor operation at inlet temperatures below 550°C. The heat loss due to backside reforming reactions as well as heat transfer to the reforming flow minimizes the effectiveness of the Pd-based catalyst for CH<sub>4</sub> combustion at lower temperatures. At higher inlet temperatures, the risk of catalyst deactivation due to surface temperatures > 800°C becomes significant. Since 600°C is approximately the highest sustainable inlet temperature for a recuperative gas turbine cycle [32], these results suggest that an alternative Pd-based hexa-aluminate catalyst with reduced high-temperature deactivation is needed for operation of CH<sub>4</sub> combustion at high temperatures in the integral reactor.
- 2) H<sub>2</sub> catalytic combustion on the Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts provides extremely stable combustion for a range of  $\phi$  in combination with backside reforming reactions. H<sub>2</sub> can also be used to heat the reactor from very low temperatures (< 200°C) to provide adequate combustion with significant amounts of backside endothermic steam reforming at a range of reactor operating temperatures from 600 to 800°C. These results indicate that the integral reactor is well suited for burning fuel cell anode exhaust in fuel cell / gas turbine cycles.
- 3) Rh-based reforming catalysts provide the necessary activity at temperatures below 800°C to control combustion catalyst temperatures for combustion  $\phi$  where otherwise high-temperature combustion catalyst deactivation would occur. This result is particularly significant in establishing the value of the integral reactor for sustaining catalytic combustion at low temperatures and for providing extremely good volumetric efficiency for H<sub>2</sub> production.
- 4) The most important reactor design parameters for assessing reactor performance are the following: reactor inlet temperature, ratio of fuel flows for combustion and reforming, combustion  $\phi$ , catalyst loading for both the combustion and reforming channels, and reactor geometry for adequate mass transfer to the surface. Steam to carbon ratio of the

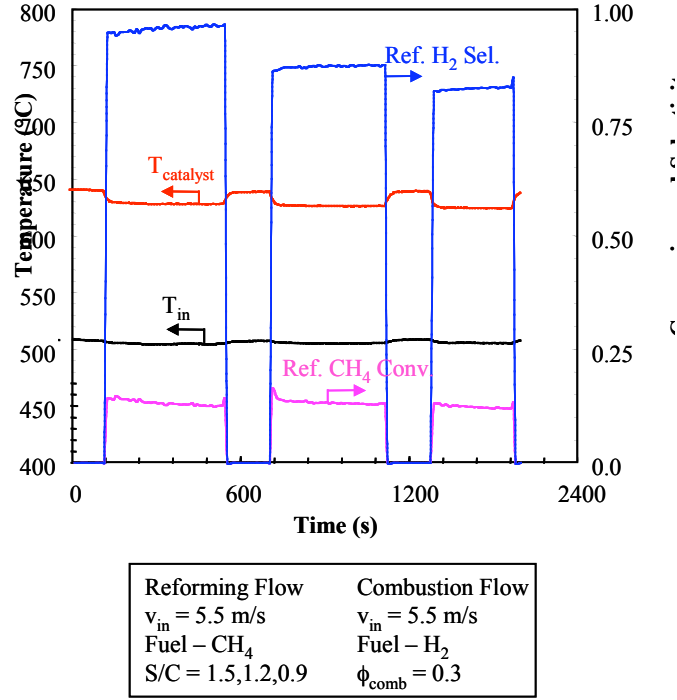
reforming flow (provided that it is adequately high to avoid coking in reforming channels) plays a minor role in determining reforming fuel conversion although as expected it did influence H<sub>2</sub> selectivity for the reformat product.

Further elaboration of summarized results 2 through 4 above are provided in the following paragraphs.

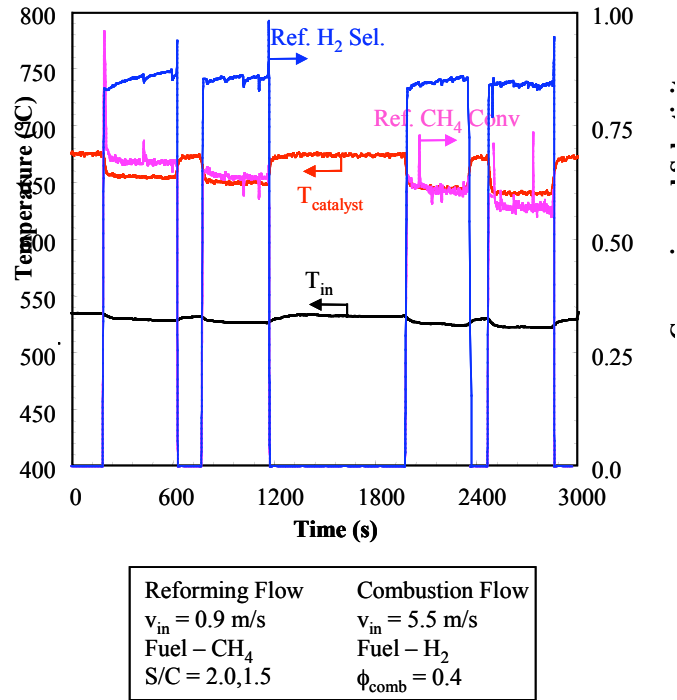
H<sub>2</sub> combustion on the Pd-catalyst was shown to drive rapid CH<sub>4</sub> steam reforming on the supported Rh catalysts at intermediate reactor temperatures. As the reactor heated up to temperatures > 600°C, H<sub>2</sub> catalytic combustion burned in a mass-transfer limited regime where combustion occurred as fast as H<sub>2</sub> was transported to the surface. Under such conditions, the heat transfer to the backside steam-reforming catalyst was calculated to be 10 times higher than if the H<sub>2</sub> was burned upstream and the adiabatic combustion products were then flowed through the combustion channel. This increase in heat transfer provides stable steam reforming at reactor temperatures that are relatively cool (600 - 700°C) compared to typical steam reformers. Results in Figure 5 show sample tests of the steam reforming with surface temperatures, conversion of CH<sub>4</sub> and selectivity of H<sub>2</sub> in the reforming stream. It should be pointed out that the reactor was not designed to achieve complete CH<sub>4</sub> but rather to provide operability information. (A reactor with higher surface-area-to-volume ratio will provide complete conversion and will be designed for future prototype development.) Nonetheless, the results show that for relatively low catalyst temperatures (~ 650°C), high conversion can be obtained at low reforming flows with very good H<sub>2</sub> selectivity. The low surface temperatures allow for higher H<sub>2</sub> selectivity based on thermodynamic equilibrium.

Figure 5 illustrates the ability for the endothermic reforming and the back-side heat transfer associated with the reforming flow to provide adequate cooling for the combustion catalyst to operate within the limits of conventional Pd-catalysts at relatively high combustion  $\phi$  for catalytic combustion. Under adiabatic conditions, the  $\phi$  of 0.3 and 0.4 in Figure 5 would provide excessively high surface temperatures for the Pd catalyst above 1000°C. However, the steam-reforming with the high activity of Rh provides the cooling needed particularly near the front end of the catalyst where combustion rates are also highest. The temperature shown in the plots in Figure 5 are near the center of the 5.5 cm length of the catalyst. Temperatures on both sides of the flat-plate at the same length from the inlet were within 5 degrees of each other. Maximum temperatures were generally observed near the front of the catalyst during H<sub>2</sub> combustion and near the end of the reactor for CH<sub>4</sub> combustion. In both cases, maximum heat release occurred near the inlet of the catalytic region of the reactor. Matching the location of maximum heat release with maximum steam reforming rates suggests that the preferred integral reactor would involve a co-flow arrangement since maximum reaction rates should occur near the same location of the separating wall. Because of this all tests performed in this study and all modeling results utilized a co-flowing configuration.

Numerous results were obtained for simultaneous H<sub>2</sub> catalytic combustion / CH<sub>4</sub> steam reforming, but only a few highlights are discussed here. The most important parameter for dictating reforming rates was the ratio of combustion fuel to reforming fuel. Figure 6 illustrates how reforming fuel conversion increases with the combustion fuel to reforming fuel ratio as expected. In a commercial application, this ratio for H<sub>2</sub> combustion and CH<sub>4</sub> reforming should



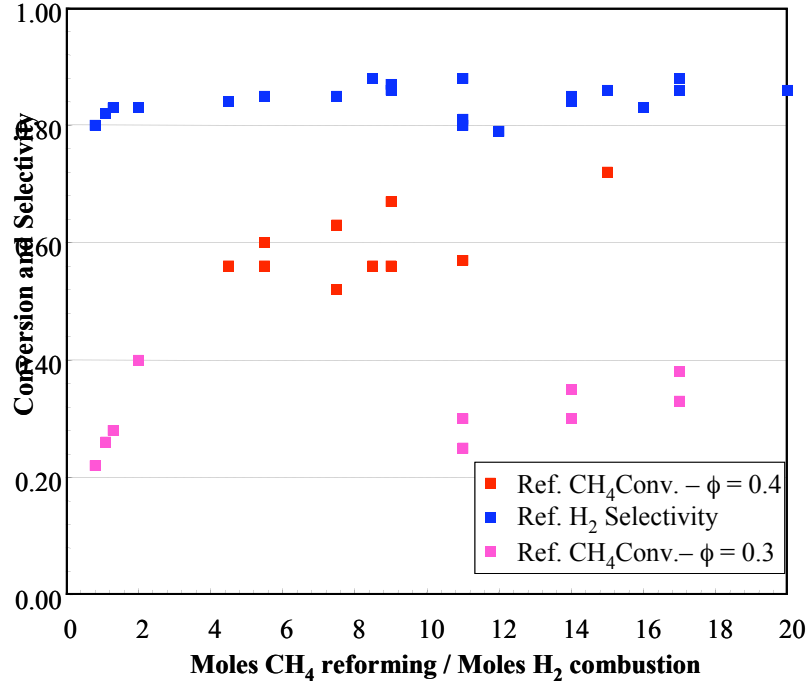
(a)



(b)

**Figure 5** – Samples of experimental results from integral  $\text{H}_2$  catalytic combustion with  $\text{CH}_4$  steam reforming showing (a) low conversion / high selectivity with high reforming flows and (b) high conversion / high selectivity with low reforming flows.





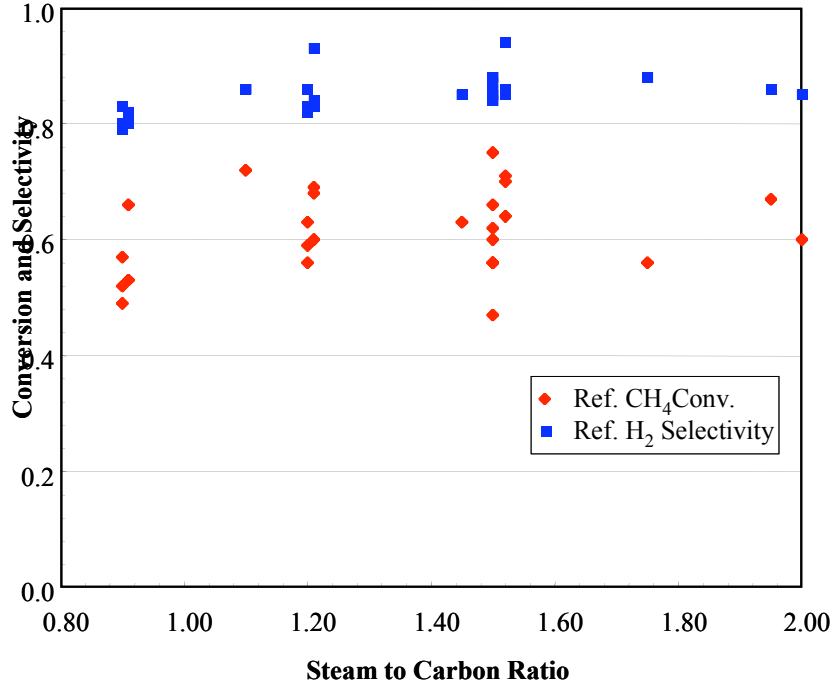
**Figure 6** – Reforming fuel conversion and H<sub>2</sub> selectivity for a range of reforming fuel to combustion fuel ratios for  $\phi = 0.3$  and  $\phi = 0.4$  and  $T_{in}$  from 525 to 575°C.

range between 1 to 2 moles of H<sub>2</sub> burned to moles of CH<sub>4</sub> reformed. The flat-plate reactor was operated in this regime for some cases but most often at higher ratios due to the need for dilution to get accurate reformat composition analysis. Model results in the following subsection provided further indication as to the reactors ability to operate well at these lower combustion fuel to reforming fuel ratios.

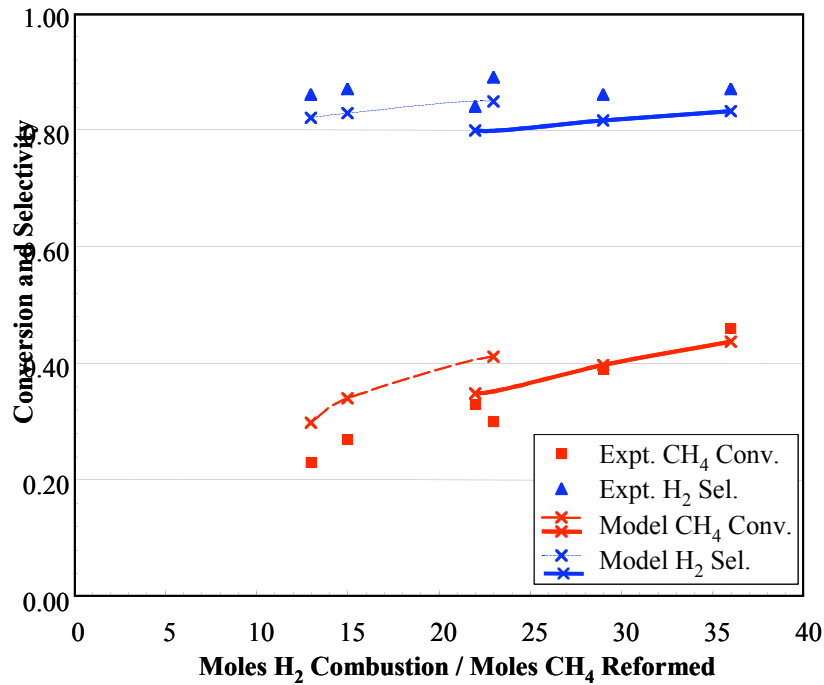
Figure 7 shows the influence of S/C ratio on reforming fuel conversion and H<sub>2</sub> selectivity for the integral steam reforming over Rh catalyst. The scatter in the conversion is due to the variation in combustion  $\phi$  and  $T_{in}$  (525°C <  $T_{in}$  < 575°C). The graph also shows the maxima in H<sub>2</sub> selectivity for S/C ratios around 0.5. This maximum results from a combination of increased cooling with the higher S/C ratios and the inadequate O for complete carbon oxidation at the lower S/C ratios. The numerous results indicate that there are favorable conditions for the integral reactor operation and these conditions were explored further through the use of validated models as discussed in the following sub-section.

#### *Results for Objective 3: Model results for reactor design*

Because of the limitations of atmospheric pressure and steam concentrations in the UMCP flat plate reactor, it was deemed critical to develop a validated numerical model for assessing how the integral reactor concept would perform at some of these conditions. In order to assure that the numerical model would capture the proper qualitative trends of global performance parameters such as CH<sub>4</sub> conversion and H<sub>2</sub> selectivity in the reformat exhaust as well as maximum surface temperature, model results using detailed surface chemistry as discussed earlier were compared to a range of experimental conditions. An example of model validation against experiments is shown in Figure 8, which compares reforming CH<sub>4</sub> conversion and H<sub>2</sub>



**Figure 7** – Influence of S/C ratio on reforming fuel conversion and H<sub>2</sub> selectivity for  $\phi = 0.3$  and  $\phi = 0.4$  and  $T_{in}$  from 525 to 575°C. All conditions shown are for high (>10) ratios of H<sub>2</sub> burned to CH<sub>4</sub> reformed.

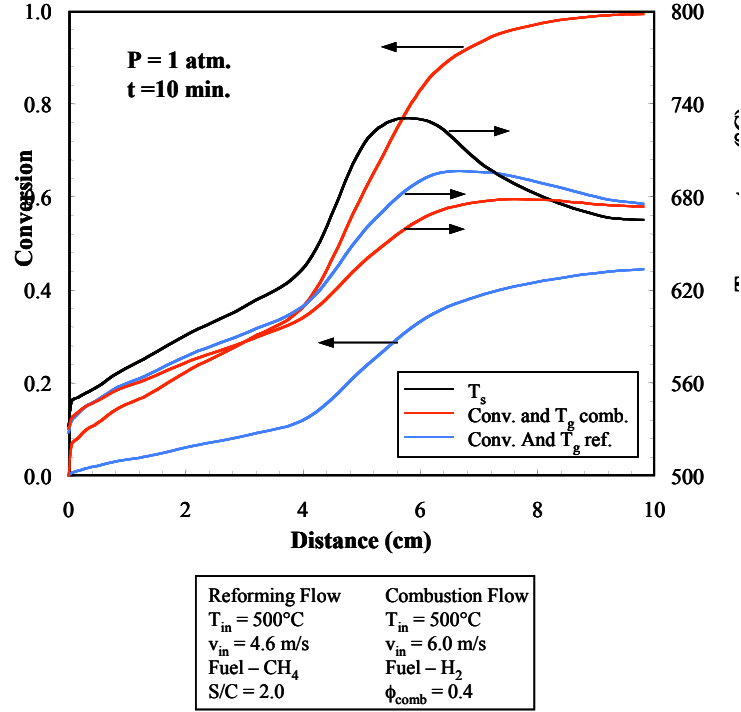


**Figure 8** – Comparison of experimental results with numerical model predictions for reforming CH<sub>4</sub> conversion and H<sub>2</sub> selectivity. The thick solid lines indicate model predictions where the experimental temperature profiles were input to the model.

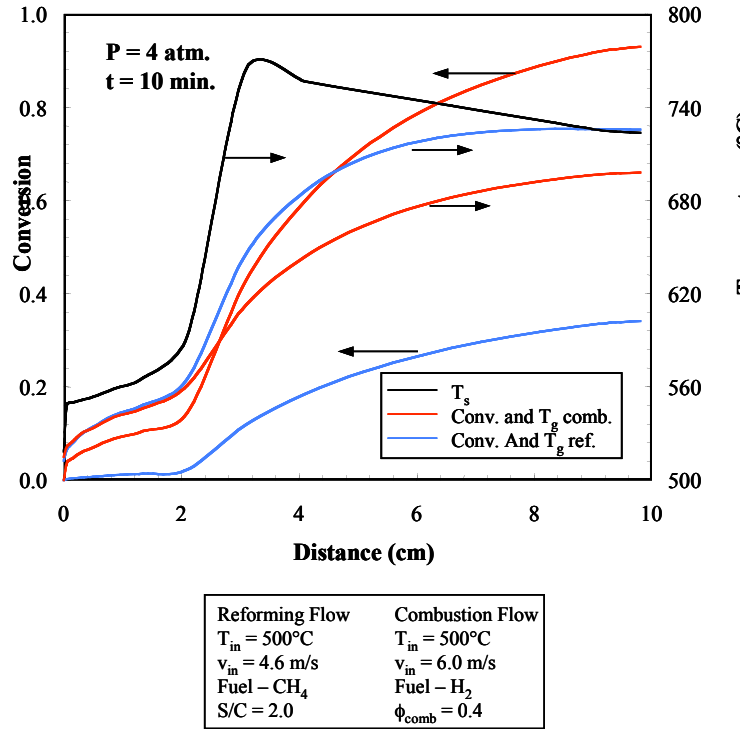
selectivity as a function of combustion flow rates for a range of reactor conditions. The results indicate that when the experimental profile was incorporated into the model (solid lines in Figure 8) the model matched to well within  $\pm 5\%$  for both conversion and  $H_2$  selectivity. These comparisons were less favorable when the temperature profiles were calculated by the model (as indicated by the dashed lines in Figure 8), but these discrepancies were largely due to heat losses in the experiment that were unaccounted for in the model. Furthermore, despite the discrepancies between the experiment and the model results with calculated temperature profiles, the model still captured the qualitative trends in reactor performance very well and as such could assess reactor performance outside of the experimental operating regime.

The transient numerical model was used to assess how a longer reactor would perform in terms at what were expected to be actual reactor operating conditions. Numerous different transient cases were run to provide the basis for a prototype reactor design. The base reactor geometry was a 10 cm reactor with 1.25 mm separation between the separating walls with 50 micron thick washcoats. The catalysts modeled in these results here were supported Rh for reforming and supported Pd for combustion. This base geometry was used to assess reactor pressure, flow inlet velocities, combustion  $\phi$ , and fuel composition. Rather than report on all of the results a brief summary of the main results from the transient modeling and their implications on reactor design and operation are given here:

- 1) Although surface reaction rates increase with pressure, they do so with pressure to the power  $< 1$ . Thus, as pressure increases, conversion in the reforming flow decreases and reactor surface temperatures increase as illustrated in comparing results shown in Figures 9a and 9b. This implies that integral catalytic combustors / steam reformers will need to be larger for high pressure cycle applications.
- 2) Reduced velocities in the combustion and reforming channels allows for significantly higher conversions in the reforming flow as indicated by comparing Figure 10 to Figure 9a. This however can result for some conditions in excessively high surface temperatures, which eventually result in the model predicting Pd-catalyst deactivation and drops in conversion. Such conditions can be avoided with adequate reforming flows as the case in Figure 10, but the high temperature deactivation becomes more difficult to avoid at higher pressure conditions suggesting increases in reforming flows is beneficial as pressure rises.
- 3) Even with heat losses at the front end, the model predicts that the reactor can rapidly heat up ( $< 1$  minute) from  $400^\circ\text{C}$  with simultaneous  $H_2$  combustion and  $CH_4$  reforming to steady state operation. The model suggests that these steady conditions are transiently stable and indicate the ability of the reactor to start up for cases where  $H_2$  is the fuel source. Similar performance was not predicted for  $CH_4$  as the combustion fuel due to the inadequate activity of  $CH_4$  as the fuel.
- 4) As with the experiments, S/C ratio plays a minor role on the reactor performance and temperature profiles. On the other hand, combustion  $\phi$  can have a large impact on reactor performance at both low and high pressures and  $\phi > 0.5$  for  $H_2$  combustion make temperature control throughout the entire reactor profile difficult for all reforming flows. Thus reactor operation is most readily controlled at  $\phi < 0.5$ .

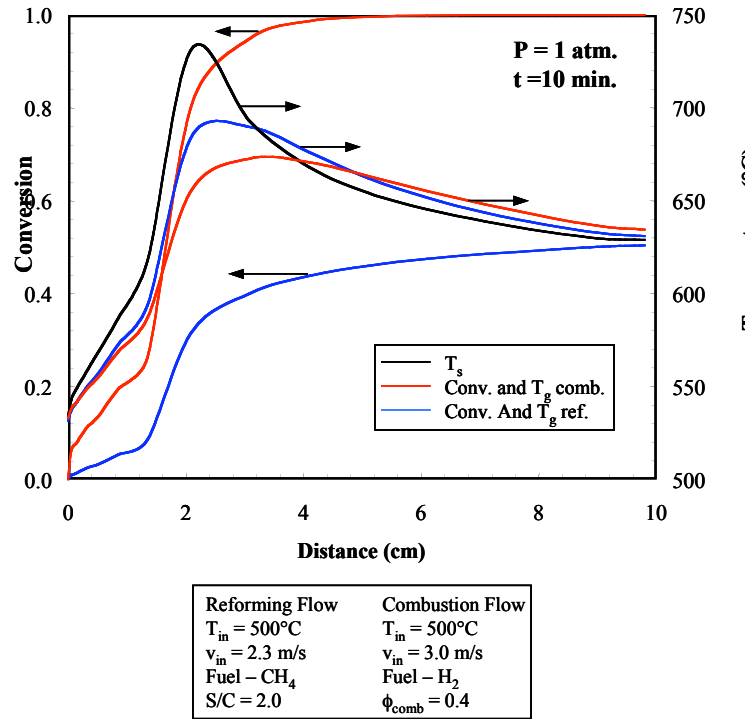


(a)



(b)

**Figure 9** – Model profiles comparing reactor surface and gas phase temperatures, reforming  $\text{CH}_4$  conversion, and combustion  $\text{H}_2$  conversion to similar conditions at (a) 1 atm and (b) 4 atm.



**Figure 10** – Model results showing increased conversion (relative to Figure 9a with reduced velocities on both sides of the reactor).

#### *Results for Objective 5: Impact of reactor in advanced fuel cell / gas turbine cycles*

Some initial analysis on how the integral reactor would impact advanced gas turbine and solid oxide fuel cell / gas turbine cycles. For the gas turbine, experimental results suggest that the use of an integral reactor to convert 5 % of a  $\text{CH}_4$  fuel stream to  $\text{H}_2/\text{CO}$  would provide the cycle the ability to provide stable combustion at conditions where sub 10 ppm  $\text{NO}_x$  is readily maintained [3,33]. While it is otherwise unclear that the integral catalytic combustor / steam reformer can improve gas turbine cycle efficiency, the analysis do suggest that efficiency improvements can be gained in solid oxide fuel cell power plants by use of an integral catalytic combustor for pre-reforming  $\text{CH}_4$  for anode  $\text{H}_2$  fuel. The efficiency gain is derived from the reduced pressure drop due to the ability for the integral reformer to operate without excess cooling air. This reduces losses from the expansion turbine of the fuel cell exhaust and thus provides a minor efficiency gain. However, more importantly the integral combustor / reformer will eliminate  $\text{NO}_x$  entirely from the reforming process (which would otherwise be produced in a gas-phase burner for a more conventional burner configuration). Quantitative aspects of these cycle improvements for the solid oxide fuel cell are not discussed here as there remain numerous uncertainties in design parameters regarding the SOFC power plants, which as of yet are not commercially available but are under development by several companies.

## **Conclusions**

The project has provided a solid basis for establishing the concept of an integral catalytic combustor / steam reformer as a means for converting natural gas into a  $\text{H}_2$  rich reformat for

fuel cells or for combustion stabilization in gas turbines. Flat plate reactor results indicate that the system can achieve stable reforming on Rh-based catalysts at temperatures that are substantially lower than typical Ni-based reformers which rely on very high temperature convective heat transfer to drive the endothermic reforming process. These results in corroboration with numerical models suggest that the best reactor design would involve a co-flow system where the high combustion and reforming rates occur near the entrance to the reactor and thus balance out the combustion heat release profile with the heat sink for the reforming reactions. The validated numerical model provides a key to further refining the reactor geometry for a prototype demonstration of a full-scale reactor for high pressure operating conditions. Based upon preliminary modeling studies, such a test should provide a successful demonstration of a volumetrically efficient manner for natural gas conversion to H<sub>2</sub>-rich syngas for ultra-clean advanced power cycles.

## Recommendations

The status of development of the proposed integral catalytic combustor / steam reformer for natural gas is by no means complete with this project. However, the results presented herein and the tools developed in this project provide the basis for establishing this reactor as a viable concept particularly for fuel cell power plants where residual H<sub>2</sub> (and CO) from the anode exhaust provide a reliable combustion fuel source for conversion. Based on the outcomes and conclusions drawn from the evaluation of this reactor concept, the following recommendations are made for further reactor development, which should be carried out by a commercial developer:

- 5) Demonstrate a prototype reactor with a Rh-based reforming catalyst for both integral CH<sub>4</sub> steam reforming with both CH<sub>4</sub> and H<sub>2</sub> catalytic combustion at pressures of 5 atm or higher. This will provide the final concept feasibility and complete the work, which was started in the current project. The University of Maryland will gladly serve as a consultant on this effort and is currently in the process of assisting one California company in their effort to demonstrate this concept reactor.
- 6) Investigate possibility of using new Pd-hexa-aluminate catalysts with higher operating temperatures than currently proposed Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in an integral reactor configuration. This should also be done in high-pressure tests where low temperature activity will be critical for reactor operability and where hexa-aluminate catalysts tend to not perform as well as their  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> counterparts.
- 7) Test for durability of preferred catalysts at cycle operating conditions. This effort, which will require commercial investment, is critical to the establishment of the final reactor design.
- 8) Develop an operation strategy for fuel cell / gas turbine power plants as well as more conventional gas turbine power plants. The need to develop a control strategy for the integral reactor is critical to its success for producing H<sub>2</sub> reliably either for a fuel cell system or for stabilization of ultra-low NO<sub>x</sub> lean-premixed combustion.

Pursuing the above recommendations will establish this reactor as a viable component for future advanced ultra-clean power plants for use in distributed power generation for a wide range of power plant sizes.

## **Public Benefits to California**

The state of California and the Energy Commission has benefited from this project as it establishes a novel approach that is now being investigated by at least one company within the state as a means for providing H<sub>2</sub> for improving operability of lean-premixed combustion systems. The ultimate success of this project in demonstrating operability of an integral reactor with stable catalyst temperatures for gas turbines with ultra-low emissions will provide a unique approach for gas turbines within California to meet BACT standards. While at this point there is no direct benefit, gas turbine market impact for distributed power generation in California will come with successful adaptation of the integral reactor for ultra-low NO<sub>x</sub> combustion systems. If further development of the integral reactor leads to commercial applications for new high-efficiency gas turbines, gas turbine manufacturers like Solar Turbines will be able to provide distributed power to California by meeting BACT standards without the prohibitive expense of SCR (or other alternatives) for exhaust gas clean-up.

Successful development of the proposed integral catalytic combustor / steam reformer for natural gas will also provide technical expertise within the state for the emerging areas of solid oxide and molten carbonate fuel cell power plants. While it is difficult to quantify how the market for high temperature fuel cells will grow, it is clear that ultra-clean power generation is currently headed in the direction of fuel cells. The development of the integral reactor concept by a California based corporation such as Solar Turbines will provide critical enabling technology within the state for the realization of these power plants of the future.

## **Development Stage Assessment**

As stated in numerous other places throughout this report, this project attempted to complete a Stage 3 development for the integral catalytic combustor / steam reformer. The project, being carried out by an academic research group, did not address many issues associated with complete commercial development such as market analysis, production readiness, and public benefits. While it is agreed that such aspects of product development are critical for commercial success, the novel nature of the proposed technology and its unique challenges merited that this project focus strictly on the engineering and technical aspects of the development effort. It was strictly in this area that the project made progress up through Stage 3. The development of the technology must now move into a Stage 4 effort for technology demonstration and begin the requisite market analysis and manufacturing cost assessment necessary for successful commercial application.

## **References**

1. G.A. Richards, M.M. McMillian, R.S. Gemmen, W.A. Rogers, and S.R. Cully, *Prog. Energy Combust. Sci.*, **27** (2001) 141.
2. W. Winkler and H. Lorenz, *J. Power Sources*, **105** (2002) 222.

3. J.N. Phillips and R.J. Roby, *Power Eng.* **104** (2000) 36.
4. G.S. Jackson, R. Sai, J.M. Plaia, C.M., Boggs, and K.T. Kiger, (2002), "Influence of Hydrogen on the Response of Lean Methane Flames to Highly Strained Flows", in press for publication in *Combust. & Flame* (2002).
5. R. Peters, E. Reinsche, and P. Cremer, *J. Power Sources*, **86** (2000) 432.
6. L.G.J. de Haart, K. Mayer K, U. Stimming, and I.C. Vinke, *J. Power Sources*, **71** (1998) 302.
7. S.T. Adelman, M.A. Hoffman, and J.W. Baughn, *J. Eng. Gas Turb. Power*, **117** (1995) 16.
8. A.L. Dicks, *J. Power Sources*, **61** (1996) 113.
9. D.L. Trimm and Z.I. Onsan, *Catal. Rev.*, **43** (2001) 31.
10. F. Joensen and J.R. Rostrup-Nielsen, *J. Power Sources*, **105** (2002) 195.
11. E.A. Polman, J.M., Der Kinderen, J.M., and F.M.A. Thuis, *Catal. Today*, **47** (1999) 347.
12. Z.R. Ismagilov, V.V. Pushkarev, O.Yu. Podyacheva, N.A. Koyabkina, and H. Veringa, *Chem. Eng. J.*, **82** (2001) 355.
13. S.T. Kolaczowski, *Trans. I. Chem. Eng.*, **73**(A), (1995) 168.
14. P. Dutta, L.H. Cowell, D.K. Yee, and R.A. Dalla Betta, "Design and Evaluation of Single-Can Full Scale Catalytic Combustion System for Ultra-Low Emissions Industrial Gas Turbines", ASME Paper No. 97-GT-292 (1997).
15. R.J. Farrauto, M.C. Hobson, and T. Kennelly, *Appl. Catal. A: Gen.*, **81** (1992) 227.
16. Retallick, W.B. and Alcorn, W.R., U.S. Patent No. 5,202,303 (1993).
17. J.G. McCarty and Y. Chang, *Scripta Metallurgica et Materialia*, **31** (1994) 1120.
18. DOE Fossil Energy Technical Center, *Fuel Cells Handbook*, 5<sup>th</sup> ed., Department of Energy (2000).
19. J. Palsson, A. Selimovic, and P. Hendriksen, "Intermediate Temperature SOFC in Gas Turbine Cycles", ASME Paper No. 2001-GT-0091 (2001).
20. D. Dissanayake, M.P. Rosynek, K.C.C. Kharas, and J.H. Lunsford, *J. Catal.*, **132** (1991) 117.
21. S. Freni, G. Calogero and S. Cavallaro, *J. Power Sources*, **87** (2000) 28.
22. W. Wiese, B. Emonts and R. Peters, *J. Power Sources*, **84** (1999) 187.
23. Kramer, J.F., Reihani, S. S., and Jackson, G.S., "Low Temperature Combustion of Hydrogen on Supported Pd Catalysts" in press for publication in the *Proceedings of the Combustion Institute*, Vol. 29 (2002).
24. Fant, D., Jackson, G.S., Karim, H., Newbury, D., Dutta, P., Smith, K. and Dibble, R., *J. Eng. Gas Turb. Power*, **122** (2000) 293.
25. Zhu, H. and Jackson G.S. "Transient Modeling of CH<sub>4</sub> Combustion over Pd-based Catalysts in Monolith Reactors", Proc. of 2<sup>nd</sup> Joint Meeting of U.S. Sections of the Combustion Institute, Oakland, March, 2001.
26. Robbins, F.A., Zhu, H., and Jackson, G.S. (2002), "Transient Modeling of CH<sub>4</sub> Catalytic Combustion for Steam Reforming Applications", accepted for publication in *Catalysis Today* (2003).
27. G.A. Groppi, A. Belloli, E. Tronconi, and P. Forzatti, *Chem. Eng. Sci.*, **50** (1995) 2705.
28. Hickman, D.A. and Schmidt, L.D., *Science*, **259** (1993) 343.
29. Deutschmann, O., R. Schwiedernoch, R., L.I. Maier, L.I., and Chatterjee, D., in *Natural Gas Conversion VI, Studies in Surface Science and Catalysis* **136**, E. Iglesia, J.J. Spivey, T.H. Fleisch (eds.), p. 215-258, Elsevier, 2001.
30. Xu, J. and Froment, G.F., *AIChE J.*, **35** (1989) 89.



31. J.R. Rostrup-Nielsen, in J.R. Anderson and M. Boudart, eds., *Catalysis: Science and Technology*, Vol. 5 Springer-Verlag, New York, 1984. Lyubovsky, M. and Pfefferle, L.D., *Appl. Catal. A: Gen.*, **198** (1998) 107.
32. Dutta, P., Yee, D.K., and Dalla Betta, R.A., ASME Paper No. 97-GT-497.
33. Jackson, G.S., Sai, R., Plaia, J.M., Boggs, C.M., and Kiger, K.T. (2002), "Influence of Hydrogen on the Response of Lean Methane Flames to Highly Strained Flows", in press for publication in *Combustion & Flame* (2003).